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(71) Applicants Montedison S.p.A., 31 Foro Buonaparte, Milan, Italy.
(72) Inventors Anacleto Dal Moro, Franco Pinamonti, Amedeo Capizzi.
(74) Agents Lloyd Wise, Tregear & Co., Norman House, 105-109 Strand, London, WC2R 0AE.

(54) **Solid formulations containing pheromones**

(57) A solid formulation comprising a sex insect pheromone as an active substance supported on an inert carrier material coated with a film-forming resin, an adhesive, a U.V. stabilizer, an antioxidant and a dispersing and/or wetting agent, the formulation having the following composition:

pheromone	0.5 to 10% by weight
film-forming resin	5 to 30% by weight
dispersing agent + wetting agent +adhesive	5 to 15% by weight
U.V. stabilizer	0.5 to 10% by weight
antioxidant	0.5 to 10% by weight
inert carrier	to make 100% by weight.

The formulations are used for the control of insects in the form of wettable powders.

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The Chemical formula appearing in the printed specification was submitted after the date of filing, the formula originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

Solid formulations containing pheromones

The present invention relates to solid formulations containing pheromones, and in particular to solid formulations containing as an active ingredient a sex pheromone of an insect supported by an inert material coated with a film-forming resin. The formulations are useful for hindering the mating of insects (mating disruption).

In recent years pheromones have become very important in the research for methods useful to control insects harmful to agricultural cultivations. Compared with conventional agents, pheromones offer the advantage of an outstanding selectivity for one species only or for a restricted number of closely related species, without affecting the other non-infesting species. Therefore it is theoretically possible to fight a certain pest with the aid of pheromones without disturbing the ecological equilibrium more than is necessary.

Pheromones are secreted outside the insect body and may be divided into classes depending on the type of reaction they induce, e.g. aggregation, tracing, sexual and alarming pheromones.

The most diffused and interesting pheromones for use in the control of insects are the sex pheromones which are most frequently secreted by females than by males, and attract the individuals of the opposite sex for mating. The use of pheromones for controlling the insects is based on the principle that small quantities of such compounds, obtained by synthesis, cause the same reactions as are induced by the male or female insects secreting the natural attractant.

In practice, the synthetized sex pheromones are used both to survey the development of the harmful species' population and to control the harmful species by mating disruption.

The former type of application permits monitoring by means of periodical samplings with small cage-traps, of the density variations of the harmful insect population in order to forecast the time in which the "harmfulness threshold" will be reached.

In the latter type of application, the sex pheromones are directed to partially or fully substitute the insecticides and to directly control the insects by modifying their behaviour (mating disruption).

There are two techniques for controlling insects using pheromones: mass trapping and confusion. The former technique (mass trapping) is directed to attract and to catch as many insects as possible by means of small cage-traps. The latter technique (confusion technique) consists in spreading the pheromone in the atmosphere in such a way as to render the males or females uncapable of "feeling" and locating the individuals of the opposite sex, so hindering mating.

In practice, the pheromone can be diffused by distributing the product at various properly spaced points of the infested area, or by uniformly spraying it on the whole cultivation. In the first case use is made of evaporators containing the pheromone, which is included or incorporated in materials of various natures suited to make volatilization occur at the proper and constant rate. However, this method is rather expensive because of the high cost of both evaporators and the labour involved.

A less expensive and complicated method is that of distributing the pheromone all over the area by spraying from the ground or from the air using special controlled-release formulations.

Slow-release formulations systems containing pheromones are known. Examples of such systems include aqueous suspensions of pheromone-containing micro-capsules having walls made of polyamides as disclosed in United States Patent Specification No. 3 577 515 or of gelatin as disclosed in United States Patent Specification No. 2 800 457 and 2 800 458; multi-layer polymeric systems containing pheromone as disclosed in A.C.S. 33, 1976 page 283, and hollow fibre systems consisting of capillaries with an open end through which the pheromone volatilizes as disclosed in United States Patent Specification No. 4 017 030.

Such systems require a sophisticated technique both for their preparation and for successive distribution in the field. A further disadvantage exhibited by some of these systems consists in supplying a release kinetics of the pheromone that is not linear, due to the structure of the capsules.

The release rate of the pheromone is not only affected by the quantity of the compound, the chemical composition of the capsules and by the chemical composition of the other formulation components, but also by environmental factors such as temperature, light and moisture. The desired requisite for a formulation that will release a sufficient quantity of pheromone to permeate the air and achieve the effect of inhibiting the mating, is a controlled, total and constant release for an adequate period of time.

The invention has been made with the above points in mind.

Therefore according to the present invention there is provided a solid formulation comprising a sex insect pheromone as an active substance supported on an inert carrier material coated with a film-forming resin, an adhesive, a U.V. stabilizer, an antioxidant and a dispersing and/or wetting agent, the formulation having the following composition:

pheromone	0.5 to 10% by weight
film-forming resin	5 to 30% by weight
dispersing agent + wetting agent + adhesive	5 to 15% by weight
U.V. stabilizer	0.5 to 10% by weight
antioxidant	0.5 to 10% by weight
inert carrier	to make 100% by weight.

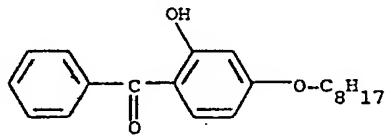
It has been observed that the formulations containing the active substance supported by an inert carrier give rise to a linear and total but fast release of the pheromone. However, formulations containing the active substance supported on inert carriers coated with film-forming resins according to the invention give rise to a controlled and total pheromone release which is approximately linear.

The release rate of the active substance is a function of both the chemical class of the chosen resin (given that for the different polymers the migration speed of the active substance is different in each case) as well as of the quantity of deposited resin.

Suitable, film-forming resins, for use in this invention, include carboxylated polyvinyl-alcohol-based compounds, compounds based on terpene polymers and mixtures of chlorinated derivatives of natural rubber.

In the formulations of the invention it is essential that a U.V. stabilizer and an antioxidant are present for protecting the chemical integrity of the active substance to enhance the stability of the pheromone in the formulation as well as to preserve the pheromone itself for as long as possible when the field treatment is carried out.

Suitable U.V. stabilizers include benzophenone derivatives having a high molecular weight. A preferred U.V. stabilizer is 2-hydroxy-4'-octyloxy-benzophenone of the formula:



Suitable antioxidants include derivatives of 2,6-di-terbutylphenol, e.g. stearyl 2,6-di-terbutylphenol propionate and pentaerythrite 2,6-di-terbutylphenol propionate.

Examples of wetting agents and adhesives suitable for use in the formulations are compounds based on mixtures of methacryl polymer and nonylphenol poly-oxyethylates; suitable dispersing agents are compounds based on sodium ligno-sulphonate.

The formulations of this invention may be prepared by conventional mixing techniques.

The formulations of this invention may be applied as a wettable powder by conventional methods for application to agricultural cultivations.

The sexual pheromones for use as the active substance in the formulatings of the invention include pheromones of different insects, e.g. (E)-11-tetradecenale, pheromone of Choristoneura fumiferana; (E,E)-8, 10-dodecadienol, pheromone of Laspeyresia pomonella L.; (Z)-8-dodecylacetate, pheromone of Grapholitha molesta, Busk.; (Z)-9-dodecenyl acetate, pheromone of Clysia ambiguella Hb.; (E,Z)-7,9-dodecadienyl acetate, pheromone of Lobesia botrana Den & Schiff; (Z)-11-tetradecenyl acetate and (E)-11-tetradecenyl acetate, pheromone of Archips podanus Scop.; (Z-E)-9,11-tetradecadienyl acetate, pheromone of Spodoptera littoralis Boisd.; (Z)-11-hexadecen-1-ale, pheromone of Heliothis armigera HB., (Z,E)-7,11-hexadecadienyl acetate; and (Z,Z)-7,11-hexadecadienyl acetate phermone of Pectinophora gossypiella.

Suitable inert carrier materials on which the active ingredient is supported include calcined fossil meal, kaolin, micronized attapulgites and talc. The fossil meal comprises a composition based on Al, Fe, Ca, Mg, Na, K silicates and is available under the trade names Celite SSC and Celite 209. Kaolin comprises compositions based on aluminum silicate and is available under the trade name Argirek B22. Attapulgite comprises compositions based on Al, Mg, Ca, Fe, Na, K silicates and is available under the trade name Diluex.

Preferred formulations in accordance with the invention having the following compositions:

pheromone	5% by weight
film-forming resin	15% by weight
dispersing agent	5% by weight
adhesive	10% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	55% by weight.

pheromone	5% by weight
film-forming resin	30% by weight
dispersing agent	5% by weight
adhesive	10% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	40% by weight.

pheromone	5% by weight
film-forming resin	20% by weight
dispersing agent	5% by weight
adhesive	10% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	50% by weight

The formulations of the invention have the advantage that they may be applied by methods and equipment already used for wettable powders, with appreciable economical advantages and ease of handling for any user.

The invention will now be illustrated by the following Examples.

EXAMPLE 1

This Example illustrates the tests for determining the most suited stabilizers.

100 g of the compositions from 1 to 10 as reported in Table I, were prepared by precipitating from a solution in CH_2Cl_2 the active substance (a.s.) and selected stabilizers on a pre-selected carrier and thereafter allowing the solvent to evaporate.

50 g of such compositions were maintained for 14 days at room temperature and 50 g of the compositions were kept at a thermostatically stabilized temperature of 40°C. At the end of this period the residual a.s., after extraction with *n*-hexane, was evaluated by gas liquid chromatography.

TABLE I

Components	Compositions										
	1	2	3	4	5	6	7	8	9	10	
(Z,E)-9,11 C_{14}Ac (a.s.) (1)	5	5	5	5	5	5	5	5	5	5	
Clortex 70 (2)	95			15			15				
Vinavil C4 (3)		95			15						
Picolite S85 (4)			95			15		15			
UV 531 (5)							5	5		5	
Irganox 1010 (6)							5	5		5	
Celite SSC (7)				80	80	80	70	70	95	85	
Degradation % after 14 days at:											
room temperature	9.1	12.3	6.2	24.8	31.4	7.3	< 0.1	< 0.1	83	< 0.1	
40°C	23.6	33.5	18.4	28.2	35.2	10.1	< 0.1	< 0.1	82	< 0.1	

Notes to Table I

(1) Pheromone of Spodoptera littoralis (Z,E)-9,11-tetra-decadienyl acetate.
(2) Clortex - registered trade mark of Caffaro, mixtures of chlorinated derivatives of natural rubber.
(3) Vinavil C4 - registered trade mark of Montedison, carboxylated polyvinylalcohols.
(4) Picolite S 85 - registered trade mark of Chem-Plast, terpene polymers.
(5) U.V. 531 - 2-hydroxy-4-*n*.octyloxybenzophenone.
(6) Irganox 1010 - pentaerythrite 2,6-di-terbutylphenol-propionate.
(7) Celite SSC - registered trade mark of Johns-Manville, fossil meal.

The samples 7, 8 and 10 were subjected to a U.V. radiation test under the following conditions:
Solar spectrum lamp with emission of U.V. radiation;
distance of samples from the lamp = 20 cm;
temperature = 40°C.

After certain periods of time part of the sample was withdrawn and the residual active substance was evaluated, after extraction with *n*-hexane, by liquid gas-chromatography. The results are recorded in Table II.

TABLE II

Sample No.	a.s. residue % after time of exposure		
	minutes		
	0	1440	2280
7	100	67.8	49.6
8	100	66.3	37.8
10	100	44.1	8.0

EXAMPLE 2

Release tests of (Z,E)-9,11 C_{14}Ac stabilized with Celite SSC and with compositions based on Celite SSC with film-forming resin.

100 g of compositions 11, 12 and 13, reported in Table III, were prepared by precipitating from a solution in CH_2Cl_2 the a.s., the stabilizers and the film-forming resin onto the powdery carrier and thereafter allowing

the solvent to evaporate. The samples reported in Table III were then exposed in a suitable cell to the following conditions:

temperature = 30°C
artificial lighting or 15 hours in 24 hours;
air change: 160 m^3/h corresponding to 6 total changes per hour of the air in the cell.

At certain periods of time part of the exposed samples were withdrawn and, after extraction with *n*-hexane, the percentage of residual a.s. was determined. The results are recorded in Table IV below.

TABLE III

Components % by weight	Compositions 11	12	13
(Z,E)-9,11 C_{14} Ac	5	5	5
U.V. 531	5	5	5
Irganox 1010	5	5	5
Clortex 70	-	10	-
Picolite S85	-	-	10
Celite SSC	85	75	75

TABLE IV

Data of the release tests

Sample No.	a.s.: % of residue after time of exposure (hours) 0	30	118	169	300	430	500
11	100	93.7	75.8	67.0	41.2	16.8	0.0
12	100	98.1	93.1	94.0	81.5	73.77	70.0
13	100	97.7	88.6	85.3	75.0	68.5	57.3

EXAMPLE 3

Preparation of complete formulations

100 g of formulations 14, 15 and 16, reported in Table V, were prepared by precipitating from a solution in CH_2Cl_2 the a.s., the stabilizers and the resin onto the powdered carrier. Thereupon the solvent was allowed to evaporated at room temperature and the wetting agent, dispersing agent and adhesive and admixed to the composition. The resulting mixture was then homogenized by passing it through a suitable mechanical mixer.

TABLE V

Components	Formulations 14	15	16
(Z,E)-9,11 C_{14}Ac	5	5	5
Irganox 1010	5	5	5
U.V. 531	5	5	5
Clortex 70	15	30	-
Picolite S85	-	-	20
Reax 45A	5	5	5
Polymer PS50 (RP10) (2)	10	10	10
Celite SSC	55	40	50
Degradation % after 14 days:			
room temperature	<0.1	<0.1	<0.1
at 40°C	<0.1	<0.1	<0.1

Notes to Table V

(1) Reax 45A - registered trade mark of Westvaco, sodium ligno-sulphonate.

(2) Polymer PS 50 (RP 10) - registered trade mark of ROL, mixtures of methacryl polymer and nonylphenol-polyoxyethylate.

EXAMPLE 4

Release tests for complete formulations

Release tests were carried out on formulations 14, 15 and 16 under the same conditions described in Example 2. The results thus obtained are reported in Table VI.

TABLE VI

Sample No.	a.s.: % of residue after exposure time in hours 0	95	168	264	624	1104	1224
14	100	94.8	91.1	88.3	67.1	37.9	35.3
15	100		94.3		88.1	72.0	
16	100		90.8		79.4	59.5	

EXAMPLE 5

Confusion method test in Egypt

Using formulation 14 of Example 4 confusion tests on Spodoptera littoralis were conducted in Egypt, in the Faiyum region, locality Tamiya, for the period 8th to 30th June and 1st to 6th July 1979.

The formulation was applied on an area of 2 Feddan (1 Feddan = 4200 m^2) cultivated with cotton, at a dosage rate of 4 g of a.s./Feddan.

The formulation was applied by conventional spraying from the ground as a suspension in water at a concentration of 0.2%.

The effectiveness of the confusion was assessed by comparing the number of adult males captured by 4 traps baited with the same pheromone, one pair of which was inside the treated zone and the other pair in the untreated zone (control) adjacent to said first pair.

The results are ported in Table VII.

TABLE VII

		8.6.1979	9	10	11	12	13	14(1)	15	16	17	18	19	20	21
TREATED AREA	Trap 1	56	103	207	137	268	254	285	0	9	26	84	6	12	14
	Trap 2	36	69	19	93	159	168	382	15	139	98	127	105	55	42
	Total Captures	92	172	226	230	427	422	667	15	148	124	221	111	67	56
CONTROL	Trap 3	51	33	112	89	162	195	448	67	213	195	325	25	4	13
	Trap 4	59	77	216	229	256	147	395	36	394	281	257	246	131	186
	Total captures	110	100	328	318	418	342	843	103	610	476	582	271	135	199
Temperature °C	max.	35	33	35	37	40	42	40	39	39	40	41	43	43	43
	min.	21	23	21	22	22	22	23	23	23	22	23	24	25	24
Relative humidity	%	49	59	42	44	32	36	34	35	38	35	48	42	42	40

(1) : day of the starting of the treatment carried out during evening hours

TABLE VII Contd.

		22	23	24	25	26	27	28	29	30	1.7.1979	2	3	4	5	6
TREATED	Trap 1	6	3	5	21	10	1	3	3	2	0	0	3	0	0	0
	Trap 2	0	0	6	28	6	4	7	0	0	0	0	1	0	0	0
AREA	Total captures	6	3	11	49	16	5	10	3	2	0	0	4	0	0	0
CONTROL	Trap 3	13	12	26	2	11	5	7	0	3	0	0	2	1	3	2
	Trap 4	98	62	45	264	145	38	27	5	12	4	5	7	12	15	16
	Total captures	111	74	71	266	156	43	34	5	15	4	5	9	13	18	18
Temperature °C	max.	42	41	45	45	45	43	43	40	40	39	41	38	41	41	42
	min.	23	24	26	24	23	22	22	21	22	21	20	21	22	21	21
Relative humidity	%	46	42	42	52	52	49	48	50	42	42	50	50	44	44	46

EXAMPLE 6

Adopting the procedure described in Example 3 the formulations reported in Table VIII were prepared.

TABLE VIII

Components	17	18
(E,E)-8,10 C_{12}, OH (1)	5	5
U.V. 531	5	5
Irganox 1010	5	5
Celite SSC	60	60
Clortex 70	10	-
Picolite S85	-	10
PS 50 (RP 10) polymer	10	10
Reax 45A	5	5

Note to Table VIII

(1) Pheromone of Laspeyresia pomonella.

Release tests were carried out with samples of formulations 17 and 18 under the same conditions described in Example 2. The results are recorded in Table IX.

TABLE IX

Sample No.	a.s.: residual % after exposure time in hours						
	0	30	96	230	400	660	1260
17	100	99.5	91.7	92.8	82.6	71.7	47.4
18	100	96.4	93.1	92.2	88.4	77.5	56.0

EXAMPLE 7

Adopting the same procedure as in Example 3 formulations 19 and 20 reported in Table X were prepared.

TABLE X

Components	19	20
(Z)-11-hexadecen-1-ale (1)	5	-
(E)-11-tetradecen-1-ale (2)	-	5
U.V. 531	5	5
Irganox 1010	5	5
Celite SSC	55	55
Clortex 70	15	15
PS 50 (RP 10) polymer	10	10
Reax 45A	5	5

Note to Table X

(1) Pheromone of Heliothis armigera.

(2) Pheromone of Choristoneura fumiferana.

Release tests were carried out with formulation 19 under the same conditions as in Example 2. The results are recorded in Table XI.

TABLE XI

Sample No.	a.s.: residual % after exposure time in hours					
	0	75	195	410	570	875
19	100	93.7	92.1	67.9	64.7	46.6

CLAIMS

1. A solid formulation comprising a sex insect pheromone as an active substance supported on an inert carrier material coated with a film-forming resin, an adhesive, a U.V. stabilizer, an antioxidant and a dispersing and/or wetting agent, the formulation having the following composition:

pheromone	0.5 to 10% by weight
film-forming resin	5 to 30% by weight
dispersing agent + wetting agent + adheisve	5 to 15% by weight
U.V. stabilizer	0.5 to 10% by weight
antioxidant	0.5 to 10% by weight
inert carrier	to make 100% by weight.

2. A formulation as claimed in Claim 1, in which the active substance is present in an amount of about 5% by weight.

3. A formulation as claimed in Claim 1 or Claim 2, in which the active substance is (Z-E)-9,11-tetradecadienyl acetate, pheromone of Spodoptera littoralis.

4. A formulation as claimed in Claim 1 or Claim 2, in which the active substance is (E,E)-8,10-dodecadienol, pheromone of Laspeyresia pomonella.

5. A formulation as claimed in Claim 1 or Claim 2, in which the active substance is (Z)-11-hexadecenal, pheromone of Heliothis armigera.

6. A formulation as claimed in Claim 1 or Claim 2, in which the active substance is (E)-11-tetradecenal, pheromone of Choristoneura fumiferana.

7. A formulation as claimed in any preceding claim, in which the film-forming resin comprises a mixture of terpene polymers or chlorinated derivatives of natural rubber.

8. A formulation as claimed in any preceding claim, in which the film-forming resin is present in an

amount in the range from 15 to 25% by weight.

9. A formulation as claimed in any preceding claim in which the U.V. stabilizer is a derivative of 2-hydroxy-4-alkoxy-benzophenone.

10. A formulation as claimed in Claim 9 in which the U.V. stabilizer is 2-hydroxy-4'-octyloxybenzophenone.

11. A formulation as claimed in any preceding claim, in which the antioxidant is a derivative of 2,6-di-terbutyl-phenol.

12. A formulation as claimed in Claim 11 in which the antioxidant is 2,6-di-terbutylphenol propionate of pentaerythrite or 2,6-di-terbutylphenol propionate of stearyl.

13. A formulation as claimed in Claim 1 comprising:

pheromone	5% by weight
film-forming resin	15% by weight
dispersing agent	5% by weight
adhesive	5% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	55% by weight.

14. A formulation as claimed in Claim 1, comprising:

pheromone	5% by weight
film-forming resin	30% by weight
dispersing agent	5% by weight
adhesive	10% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	40% by weight.

15. A formulation as claimed in Claim 1, comprising:

pheromone	5% by weight
film-forming resin	20% by weight
dispersing agent	5% by weight
adhesive	10% by weight
U.V. stabilizer	5% by weight
antioxidant	5% by weight
inert carrier	50% by weight.

16. A formulation as claimed in any preceding claim in the form of a wettable powder.

17. A formulation as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.

18. A method for the control of harmful insect species, which comprises applying a formulation as claimed in any preceding claim over the infested area.

19. A method as claimed in Claim 18 substantially as herein described with reference to Example 5.

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